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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

This invention relates to use of the BISUHOSU fit as ligand in a BISUHOSU fit and its metal complex, its manufacture, and catalytic reaction.

[0002]

The reaction to more aldehydes of a carbon atom between the olefin compound under existence of a catalyst, a carbon monoxide, and hydrogen is well-known as a hydroformylation (oxo-**). An element's compound especially rhodium, and cobalt compound of a periodic system of transition metals are often used as a catalyst at this reaction. [of a VIII group] As compared with the catalysis by cobalt, the advantage of higher selectivity usually arises by the hydroformylation using a rhodium compound, as a result, in many cases, it is more economical. In the case of the hydroformylation in which a catalyst is carried out by the rhodium, the complex which serves as a rhodium from trivalent phosphorus compounds advantageously as ligand is used mostly. Well-known ligand is a compound from the class of a phosphine, HOSUFITTO, and phospho knitting. The good outline about the technical level of the hydroformylation of an olefin is looked at by for example, B.CORNILS, W.A.HERRMANN, "Applied Homogeneous Catalysis with Organometallic Compounds", the 1&2nd volume, VHC, Weinheim, New York, and 1996.

[0003]

Each catalyst system (cobalt or rhodium) has the characteristic advantage. Therefore, according to the use matter and the purpose product, a different catalyst system as the following examples show is used. When working using a rhodium and triphenyl phosphine, an alpha olefin can be hydroformylated by the comparatively low pressure. As Lynn content ligand, it is superfluous and triphenyl phosphine is usually used, and in order to raise the selectivity of a reaction even to n-aldehyde product for which it asks commercially in that case, high ligand / rhodium ratio are needed.

[0004]

Patents US4694109 and US4879416 have indicated the use in the hydroformylation of the olefin in bis-phosphine ligand and low synthetic gas pressure. Especially in the case of the hydroformylation of a propene, high activity and high n/i-selectivity are attained using this type of ligand. The use especially in a hydroformylation reaction in the phosphine ligand and catalytic reaction of two seats is indicated by WO 95/30680. The bis-phosphine by which the ferrocene bridging was carried out is indicated by the patent reference US4169861, US4201714, and US4193943 as ligand for a hydroformylation.

[0005]

The fault of the phosphine of two seats is comparatively high cost needed for the manufacture. Therefore, often using such a system in a industrial process does not pay well.

[0006]

Although it is a suitable catalyst in order that a rhodium-MONOHOSU fit-complex may hydroformylate the olefin of the shape of a branched chain which has the double bond which exists in the interior, the selectivity for the compound which has oxygen at the end is slight. Use of the MONOHOSU fit by which the bis-arylene permutation of [at the time of hydroformylating a steric hindrance olefin, for example, isobutene, according to a rhodium catalyst] was carried out from

EP0155508 is well-known.

[0007]

It is only that the olefin of the shape of a branched chain which has the double bond which a rhodium-BISUHOSU fit-complex carries out the catalyst of the hydroformylation of a straight chain-like olefin which has the double bond which exists in an end and the interior, and the product by which the hydroformylation was carried out mainly at the end at that time arises, and exists in the interior to this reacts slightly. Although this HOSUFITTO produces the catalyst of the activity which improved when coordination was carried out centering on transition metals, the useful-life-longevity behavior of this catalyst system is especially dissatisfied based on the hydrolysis susceptibility of HOSUFITTO ligand. The remarkable improvement was able to be attained by using the bis-aryl diol permuted by EDAKUTO for HOSUFITTO ligand as indicated by EP0214622 or EP0472071.

[0008]

According to the reference, the rhodium complex of such ligands is a hydroformylation catalyst [very activity / for an alpha olefin]. PORIHOSU fit ligand is indicated by patents US4668651, US4748261, and US4885401, and 2-butene can be made to react to an end with high selectivity again to an alpha olefin or the product which has oxygen using this ligand. The ligand of this type of two seats was used also for the hydroformylation of a butadiene (US5312996).

[0009]

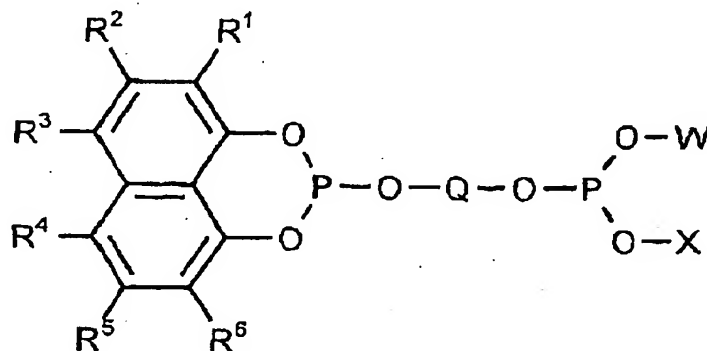
Although the aforementioned BISUHOSU fit is the very good complex ligand for a rhodium hydroformylation catalyst, to improve the effectiveness and hydrolytic stability further is wished.

[0010]

General structure I

[0011]

[Formula 9]



[0012]

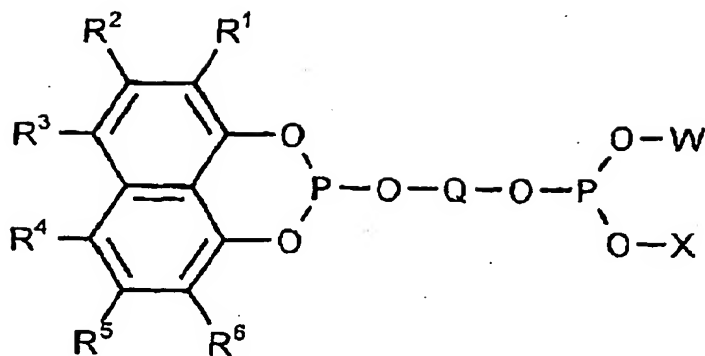
The BISUHOSU fit which **** could be manufactured easily and it became clear that it is suitable as ligand in the case of the reaction by the metal catalysis.

[0013]

Therefore, the object of this invention is a general formula I.

[0014]

[Formula 10]



[0015]

Inside of [type,

R1, R2, R3, R4, R5, R6=H, the aliphatic series that has 1-50 carbon atoms, Alicyclic, aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, The hydrocarbon group of aliphatic series-aromatic series, F, Cl, Br and I, -OR7, -COR7, -CO two R7, -CO2M, - In SR7, -SO two R7, -SOR7, -SO three R7, -SO3M, -SO2NR seven R8, NR7R8, N=CR7R8, NH2, and that case, R1-R6 have semantics which is the same or is different, and it may be carrying out covalent bond mutually,

These have semantics which is the same or is different in the hydrocarbon group of the permutation or the unsubstituted aliphatic series which has R7, R8=H, and 1-25 carbon atoms, or aromatic series, and that case,

M= alkali-metal ion, alkaline-earth-metal ion, ammonium ion, phosphonium ion,

The hydrocarbon group of the aliphatic series of bivalence which has Q= 1-50 carbon atoms, alicyclic, aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, and aliphatic series-aromatic series,

W -- X -- = -- one - 50 -- a piece -- carbon -- an atom -- having -- aliphatic series -- alicyclic -- aliphatic series - alicyclic -- heterocycle -- a formula -- aliphatic series - heterocycle -- a formula -- aromatic series -- aliphatic series - aromatic series -- a hydrocarbon group -- these -- being the same - - or -- or -- differing -- **** -- or -- or -- mutual -- covalent bond -- carrying out -- **** --] --

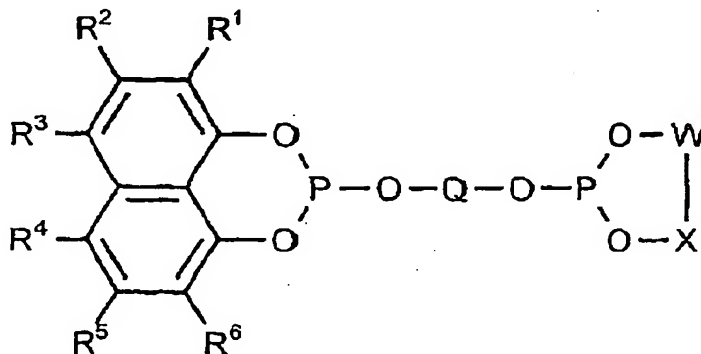
BISUHOSU -- a fit -- it is .

[0016]

The special embodiments of the BISUHOSU fit by this invention are Formulas II and III.

[0017]

[Formula 11]

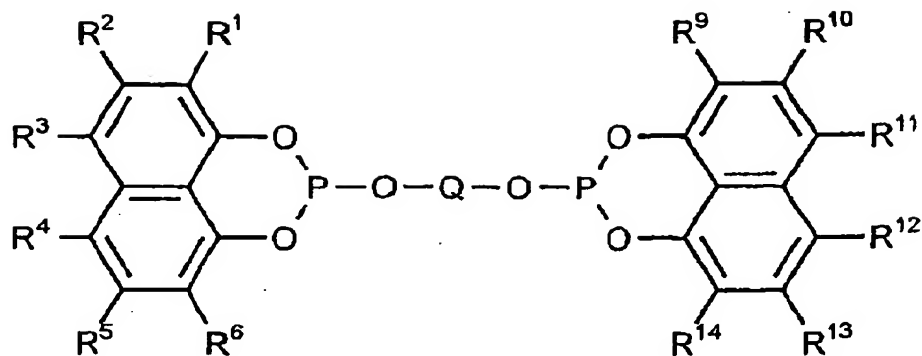


[0018]

It reaches.

[0019]

[Formula 12]



III

[0020]

Alicyclic [in which W and X have 1-50 carbon atoms among [type / the aliphatic series, alicyclic], The hydrocarbon group of aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, and aliphatic series-aromatic series is expressed. X -- and -- W -- being the same -- or -- or -- differing -- or -- or -- mutual -- covalent bond -- carrying out -- **** -- and -- R -- one -- R -- two -- R -- three -- R -- four -- R -- five -- R -- six -- R -- seven -- R -- eight -- and -- Q -- the above -- semantics -- having --] -- BISUHOSU -- a fit -- being related .

[0021]

R9, R10, R11, R12, R13, R14=H, the aliphatic series that has 1-50 carbon atoms, Alicyclic, aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, The hydrocarbon group of aliphatic series-aromatic series, F, Cl, Br and I, -OR15, -COR15, -CO two R15, -CO2M, - In SR15, -SO two R15, -SOR15, -SO three R15, -SO3M, -SO2NR 15R16, NR15R16, N=CR15R16, NH2, and that case, R9-R14 have semantics which is the same or is different, and it may be carrying out covalent bond mutually.

[0022]

M expresses alkali-metal ion, alkaline-earth-metal ion, ammonium ion, or phosphonium ion.

[0023]

Or it permuted, unsubstituted aliphatic series or an unsubstituted aromatic hydrocarbon radical is expressed, and these express a thing for which R15 and R16 are the same, or may differ, and it has H and 1-25 carbon atoms each time and which is the same or is different in that case.

[0024]

The example for Q may be the hydrocarbon group of bivalence, and this may be aliphatic series, alicyclic, aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, or aliphatic series-aromatic series. The ring structure which exists by the case may be permuted by the very thing and the above-mentioned hydrocarbon group. the structure element of the letter of opening and closing -- one or two or more methylene groups -- oxygen, sulfur, NR7, and/or NH -- and/or, one or two or more CH radicals may be replaced with with nitrogen.

[0025]

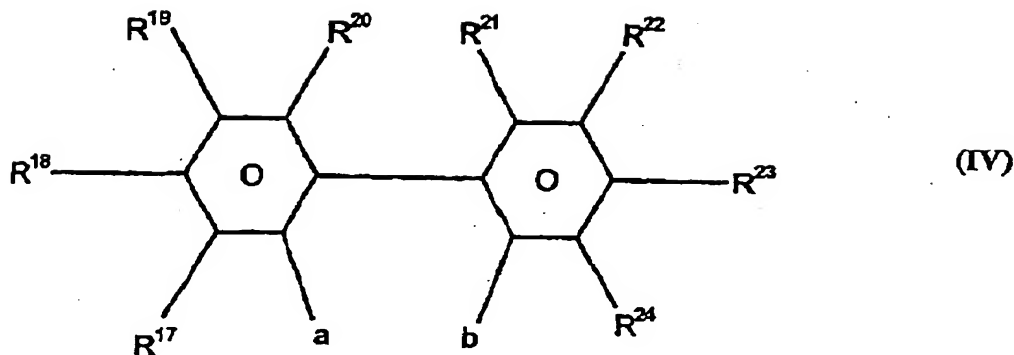
Q expresses advantageously the radical of the bivalence which has the aromatic series radical. Q may be a phenylene group, a naphthyl group, the bis-arylene radical of bivalence, or the radical of the bivalence of diphenyl ether. Furthermore, Q may have general structure-Ar-Z-Ar-. Ar expresses the aromatic series radical of the bivalence of a monocycle or many rings here. R7 and R8 may express the aliphatic series which has hydrogen and/or 1-25 carbon atoms, and/or an aromatic series radical in that case by Z expressing methylene group-CR7R8- permuted by direct coupling or the case, and you may have the hetero atom further. Furthermore, radicals R7 and R8 form one or two or more rings unitedly, that is, may have covalent bond.

[0026]

The BISUHOSU fit indicated by general formulas I, II, and III to the radical Q is a general formula IV.

[0027]

[Formula 13]



[0028]

Inside of [type,

R17, R18, R19, R20, R21, R22, R23, R24=H, The aliphatic series which has 1-50 carbon atoms, alicyclic, aliphatic series-alicyclic, a heterocycle type, The hydrocarbon group of an aliphatic series-heterocycle type, aromatic series, and aliphatic series-aromatic series, F, Cl, Br, I, -OR25, -COR25, -CO two R25, -CO2M, - In SR25, -SO two R25, -SOR25, -SO three R25, -SO3M, -SO2NR 25R26, NR25R26, N=CR25R26, NH2, and that case, R17-R24 have semantics which is the same or is different, and it may be carrying out covalent bond mutually,

The permutation or the unsubstituted aliphatic series which has R25, R26=H, and 1-25 carbon atoms, or the hydrocarbon group of aromatic series,

M= alkali-metal ion, alkaline-earth-metal ion, ammonium ion, phosphonium ion,

Locations a and b have especially an advantageous thing showing the hydrocarbon group (bis-arylene radical) of] expressed as a joint of this substituent in structure element O-Q-O in the compound of Formulas I, II, and III in that case.

[0029]

The example for W and X is the hydrocarbon group which may be aliphatic series, alicyclic, aliphatic series-alicyclic, a heterocycle type, an aliphatic series-heterocycle type, aromatic series, or aliphatic series-aromatic series. The ring structure which exists in a radical may be permuted by the very thing and the aforementioned hydrocarbon group. One or two or more methylene groups may be replaced with by oxygen, sulfur, NR7, and/or NH in the structure element of the letter of opening and closing, and/or one or two or more CH radicals may be replaced with with nitrogen.

[0030]

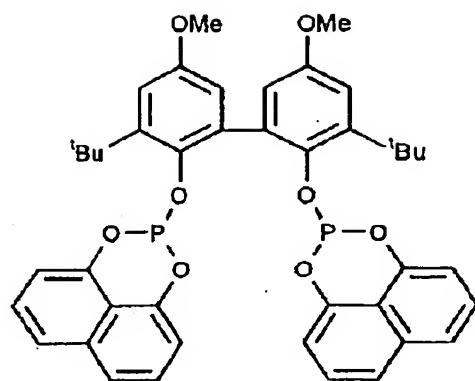
The object of this invention is also a BISUHOSU fit metal complex containing one or two or more BISUHOSU fits of the metal of the 4th, 5, 6 and 7, or the 8 vice-group of the periodic system of an element, and Formulas I, II, or III. The substituent (R1-R24, Q, X, W) of these BISUHOSU fits expresses what was already indicated.

[0031]

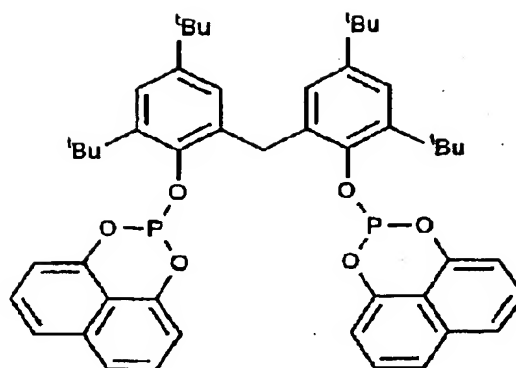
Although the typical example of the ligand of the general formulas I, II, and III in the range of this invention is indicated below, the protection range of this invention is not limited by this.

[0032]

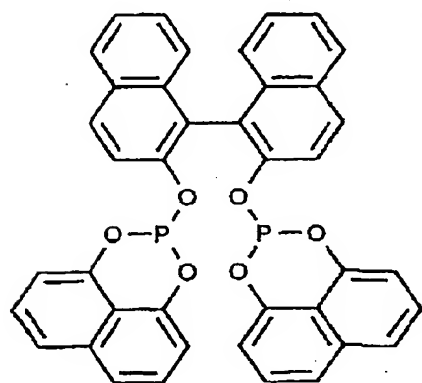
[Formula 14]



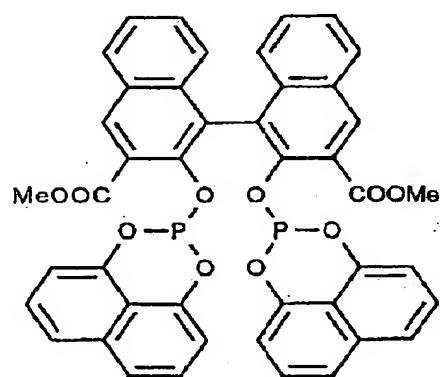
1a



1b

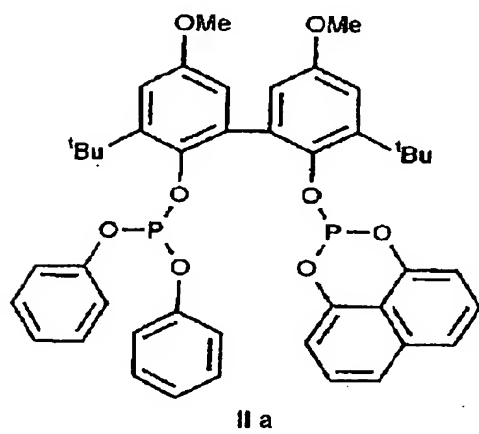
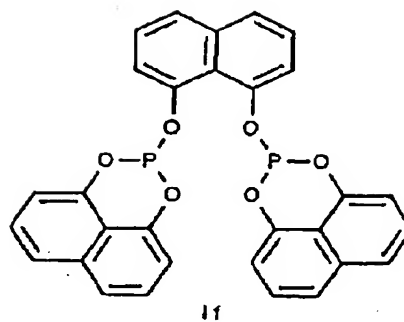
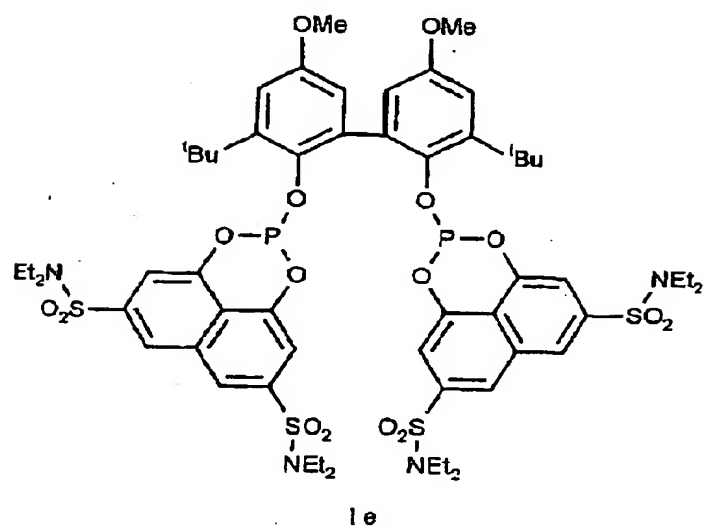


1c

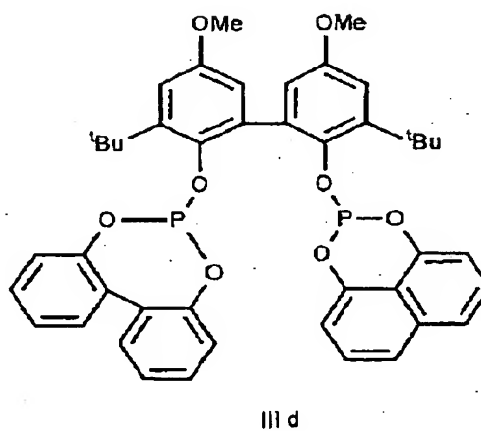
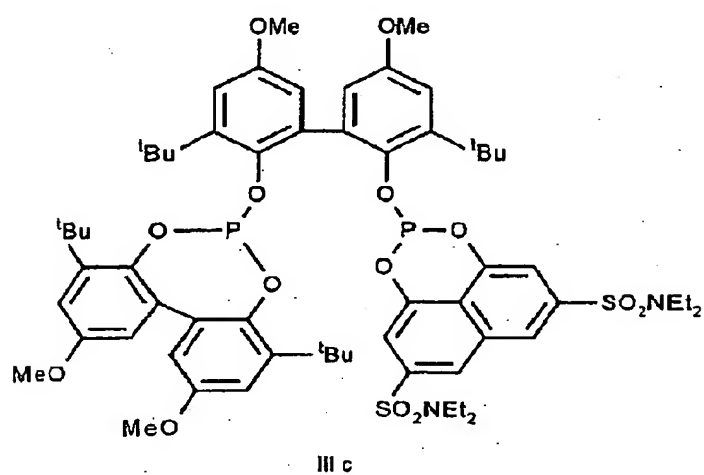
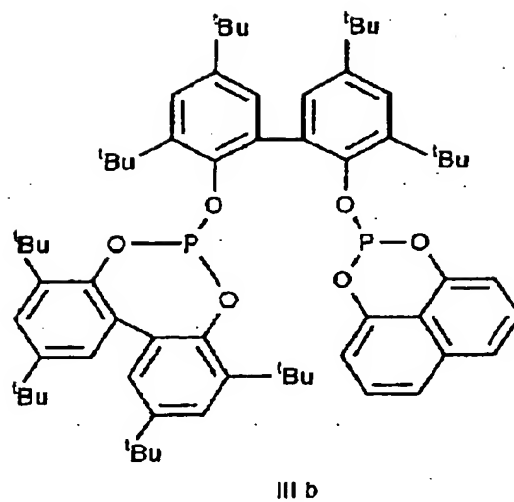
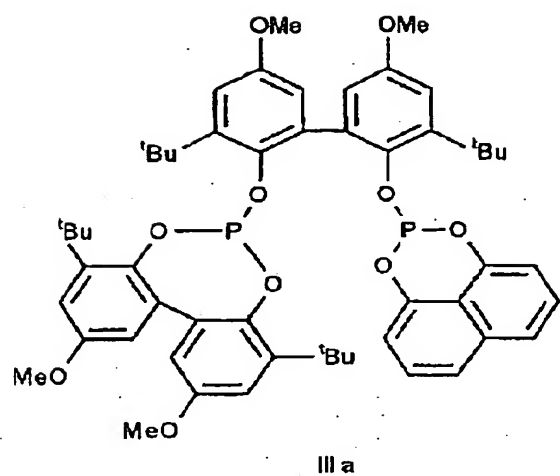


1d

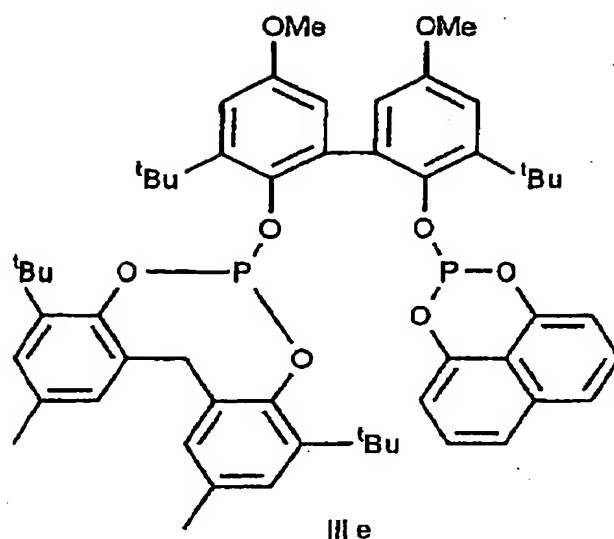
[0033]
[Formula 15]



[0034]
[Formula 16]



[0035]
[Formula 17]



[0036]

The BISUHOSU fit by this invention can be manufactured by the reaction of the Lynn halogenide and alcohol, and a halogen atom is exchanged for an alcoholate radical in that case.

[0037]

a) Lynn -- make a phosphorus trichloride and the alcohol of diol or the two-mol equivalent react to a mono-halo GENHOSU fit (intermediate product A) advantageously 3 halogenide

[0038]

b) HOSUFITTO (intermediate product B) the hydroxyl permutation was carried out [HOSUFITTO] by the reaction with diol (HO-Q-OH) is obtained from an intermediate product A.

[0039]

c) Make a phosphorus trichloride react advantageously to a phosphorus San halogenide, 1 permuted by the case, 8-dihydroxy naphthalene, and a mono-halo GENHOSU fit (C).

[0040]

d) A desired BISUHOSU fit is obtained from a reaction with intermediate products B and C.

[0041]

The symmetrical BISUHOSU fit by the general formula III can be obtained still more easily by the reaction of Component C and diol.

[0042]

Since the diol used and a subsequent product are often solid-states, generally a reaction is carried out in a solvent. As a solvent, the aprotic solvent to which diol and phosphorus compounds do not react is used. A suitable solvent is a tetrahydrofuran, diethylether, or aromatic hydrocarbon, for example, toluene.

[0043]

Hydrogen halide arises in the case of the reaction of the Lynn halogenide and alcohol, and this combines with the base added. For example, a tertiary amine, for example, triethylamine, is used. It is also possible to convert alcohol to a metal alcoholate by the reaction with sodium hydride or butyl lithium, before reacting.

[0044]

Other approaches are suitable in order to offer the BISUHOSU fit ligand by this invention further in addition to this synthetic path. Using for example, a tris (dialkylamino) phosphine (as a substitute of a phosphorus trichloride) is mentioned to this.

[0045]

1 and 8-dihydroxy naphthalene component used in composition is obtained by similarly different approach. For example, 1 and 8-dihydroxy naphthalene itself is obtained from 1 and 8-naphthalene sulfone by the reaction with a potassium hydroxide (L. 247 Ann. Chem. 1888, 356). Furthermore,

the derivative of a chromotropic acid (4, 5-dihydroxy -2, 7-naphthalene disulfon acid) is offered as EDAKUTO.

[0046]

The BISUHOSU fit by this invention of Formulas I, II, and III is a suitable component in order to manufacture metal and complex of the 4th, 5, 6 and 7, or the 8 vice-group of the periodic system of an element. especially -- the -- this complex can be used using a 8 vice-group's metal as a catalyst for a carbonylation reaction or a hydroformylation reaction (for example, the hydroformylation of C2 - a C25-olefin sake). This ligand is excellent with high hydrolytic stability. When using a rhodium especially as a catalyst metal, high catalytic activity arises in a hydroformylation reaction. Based on the high molecular weight, the BISUHOSU fit by this invention has slight volatility. Therefore, this compound is easily separable from an easy-volatility resultant. These are dissolved sufficiently good in a usual organic solvent.

[0047]

Another object of this invention is use of the BISUHOSU fit in the approach for hydroformylating an olefin and the olefin which has 2-25 carbon atoms advantageously to the ****ing aldehyde, or a BISUHOSU fit metal complex.

[0048]

In order to manufacture a catalytic activity metal complex, the metals used advantageous because of the BISUHOSU fit by this invention are a rhodium, cobalt, platinum, and a ruthenium. The ligand and the metal by this invention form an activity catalyst under a reaction condition. The ligand by this invention can be added to a reaction mixture in the form of isolation in this case. Furthermore, it is also possible to use the transition metal complex which has the above-mentioned BISUHOSU fit ligand as a precursor for an original catalytic activity complex. A hydroformylation process can be carried out by the isolation BISUHOSU fit ligand of an excessive amount in stoichiometry or, respectively.

[0049]

The ligand of the Lynn content with others suitable also for a BISUHOSU fit also according [the mixture of further various ligands] to this invention may also exist as a ligand complex of isolation.

[0050]

A phosphine, HOSUFITTO, phospho knitting, or HOSUFI knitting can be used as additional ligand which exists in a reaction mixture.

[0051]

The example of such ligand is as follows. :

Phosphine: Triphenyl phosphine, a tris (p-tolyl) phosphine, a tris (m-tolyl) phosphine, a tris (o-tolyl)-phosphine, a tris (p-methoxyphenyl) phosphine, a tris (p-dimethylamino phenyl)-phosphine, tri-cyclohexyl phosphine, a tricyclo pentyl phosphine, a triethyl phosphine, the Tori (1-naphthyl) phosphine, tribenzylphosphine, tri-n-butyl phosphine, a tree t-butyl phosphine.

[0052]

HOSUFITTO : Trimethyl HOSUFITTO, triethyl HOSUFITTO, A tree n-pro PIRUHOSU fit, a tree i-pro PIRUHOSU fit, A tree n-BUCHIRUHOSU fit, a tree i-BUCHIRUHOSU fit, a tree t-BUCHIRUHOSU fit, Tris (2-ethylhexyl) HOSUFITTO, triphenyl HOSUFITTO, Tris (2, 4-G t-buthylphenyl) HOSUFITTO, tris (2-t-butyl-4-methoxyphenyl) HOSUFITTO, tris (2-t-butyl-4-methylphenyl) HOSUFITTO, tris (p-KURESHIRU) HOSUFITTO. Furthermore, steric hindrance HOSUFITTO ligand is suitable ligand as especially indicated by EP155508, US4668651, US4748261, US4769498, US4774361, US4835299, US4885401, US5059710, US5113022, US5179055, US5260491, US5264616, US5288918, US5360938, EP471071, EP518241, and WO 97/20795.

[0053]

Phospho knitting: The hydrogen atom is replaced with with the alkyl group, the aryl group, or the halogen atom completely partially a methyl diethoxy phosphine, a phenyl dimethoxy phosphine, a FENIRUJI phenoxy phosphine, 6-phenoxy-6H-dibenzo [c, e] [1, 2] OKISA phospholine and these derivatives, and in it, and ligand is indicated by WO9843935, JP 09-268152, DE19810749, and the German patent application DE19954721 and DE19954510.

[0054]

Especially usual HOSUFI knitting ligand is indicated by US5710344, WO9506627, US5360938, or JP07082281. Examples for this are diphenyl (phenoxy)-phosphines and these derivatives, and in it, the hydrogen atom is replaced with the alkyl group, the aryl group, or the halogen atom completely partially, and are a diphenyl (methoxy) phosphine, a diphenyl (ethoxy) phosphine, etc.

[0055]
per one mol of radical VIII-transition metals -- general -- 1-500 -- 1-200, and the ligand by 3-50-mol this invention are used preferably advantageously. In order to maintain the concentration of the ligand of isolation uniformly, ligand fresh to the product at the time of the arbitration of a reaction can be added. The catalyst of the transition-metals-BISUHOSU fit complex by this invention is compoundable before the use. However, a complex [*****] is usually formed among a reaction medium from the BISUHOSU fit ligand by the catalyst precursor and this invention in a site.

[0056]
The salt or complex of transition metals is used as a catalyst precursor. The example is rhodium carbonyl, a nitric-acid rhodium, a rhodium chloride, Rh (CO)₂ (acac) (acac= acetylacetonate), an acetic-acid rhodium, an octanoic-acid rhodium, or a nonoic acid rhodium.

[0057]
the concentration of the metal in a reaction mixture -- the range of 1 ppm - 1000 ppm -- it is the range of 5 ppm - 300 ppm advantageously.

[0058]
By the well-known approach, the hydroformylation reaction carried out using the metal complex by this invention which ***** [which ***** and BISUHOSU-fits] is J. FALBE, "New Syntheses with Carbon Monoxide", Springer Verlag, Berlin, Heidelberg, New York It can carry out as indicated after York and the 95th page (1980).

[0059]
40 degrees C - 180 degrees C of reaction temperature for the hydroformylation method using the BISUHOSU fit or BISUHOSU fit metal complex by this invention are 75 degrees C - 140 degrees C advantageously as a catalyst. The pressure to which a hydroformylation advances is 15-64 bars advantageously 1-300 bars of synthesis gas. the mole ratio (H₂/CO) of the hydrogen in synthesis gas, and a carbon monoxide -- 10 / 1 - 1/10 -- it is 1 / 1 - 2/1 advantageously.

[0060]
A catalyst or ligand is dissolved in homogeneity into the hydroformylation mixture which consists of EDAKUTO (olefin) and a product (an aldehyde, alcohol, high-boiling point matter formed into a process). A solvent can be further used by the case.

[0061]
EDAKUTO for a hydroformylation is the mixture of the monoolefin which has a monoolefin or 2-25 carbon atoms, and has the C-C double bond located in an end or the interior. These may be the structures of the shape of a straight chain, the shape of a branched chain, and a ring type, and may have two or more olefin system partial saturation radicals. The example A propene, 1-butene, a c-2-butene, a t-2-butene, The mixture of isobutene, a butadiene, and a C₄-olefin, 1-, or 2-pentene, The 2-methylbutene -1, the 2-methylbutene -2, the 3-methylbutene -1, 1-, 2- or 3-hexene, the C₆-olefin mixture produced in the case of dimerization of a propene (Zypro Penn), A 1-heptene, heptene, 2-, or 3-methyl-1-hexene, 1-octene, octene, 2-methyl heptene, 3-methyl heptene, 5-methyl heptene -2, 6-methyl heptene -2, 2-ethyl hexene -1, the isomer C₈-olefin mixture produced in the case of dimerization of a butene (jib ten), 1-nonene, nonene, 2- or 3-methyl octene, the C₉-olefin mixture produced in the case of 3 quantification of a propene (TORIPUROPEN), The C₁₂-olefin mixture produced in the case of 3 quantification of a butene in the case of 3 quantification of decene, 2-ethyl-1-octene, dodecen, and a propene (a tetra-propene or TORIBUTEN), The olefin mixture manufactured by co-oligomer-ization of the olefin which has tetra-decene, hexa decene, the C₁₆-olefin mixture (tetra-butene) produced in the case of 4 quantification of a butene, and a different carbon number (advantageously 2-4), What was divided into the fraction which is the same or has a similar carbon number by the case by distillation. The olefin similarly produced by composition of Fischer Tropsch or olefin mixture, and the olefin which is obtained by oligomerization of ethene or is obtained by the metathesis reaction or the telomerization reaction can be used.

[0062]

advantageous EDAKUTO -- the dimer of a propene, 1-butene, 2-butene, 1-hexene, 1-octene, and a butene, and a trimer (jib a ten, a G n-butene, a G ISO-butene, TORIBUTEN) -- and generally it is an alpha olefin.

[0063]

A hydroformylation can be carried out continuously or nonsequentially. The example of industrial operation is a stirring container, a bubble tower, a jet-nozzle reactor (Strahlduesenreaktoren), a tubular type reactor, or a looping reactor, and a part of these are cascades-like, or may have equipment.

[0064]

A reaction can also perform carrying out consistently in two or more phases: The conventional approach, for example, rectification, can perform separation of the aldehyde compound and catalyst to produce. Technically, by distillation, a falling film mold evaporator or a film evaporator can perform this. Especially this corresponds, when separating the catalyst which is dissolving into a high boiler from the product of a low-boiling point. The separated catalyst solution can be used for the further hydroformylation. When using a low-grade olefin (for example, a propene, a butene, a pentene), it is also possible to take out a product from a reactor through a gaseous phase.

[0065]

Although the following examples explain this invention, they should not limit the applicability produced from a claim.

[0066]

EXAMPLE

All the preparation objects were carried out under protection gas with the standard rocking technique (Standard-Schlenk-Technik). The solvent was dried using the drying agent suitable before use.

[0067]

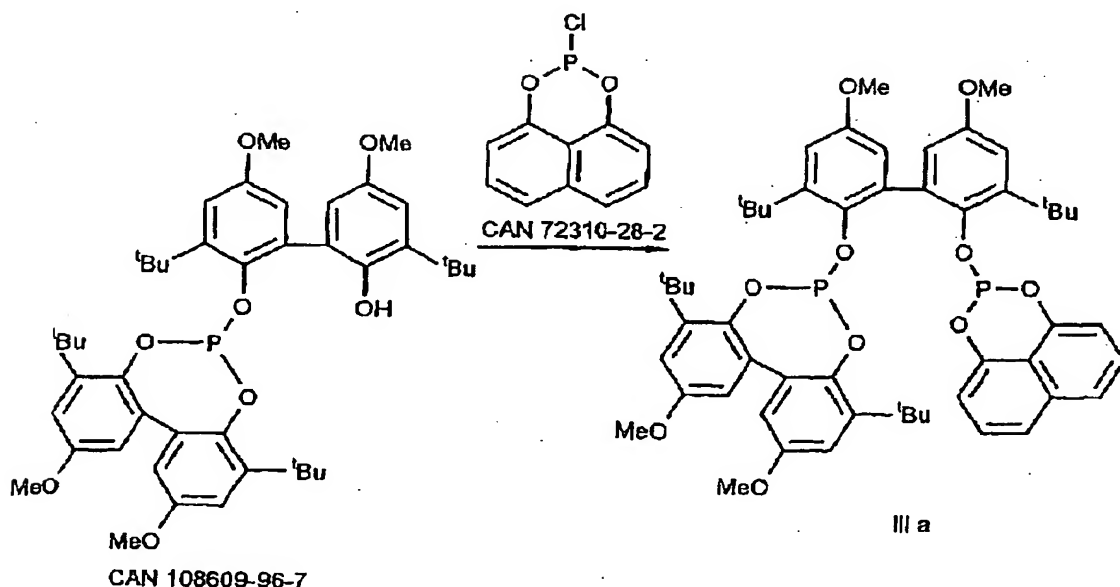
Example 1

Composition of Ligand IIIa

The hydronalium KISHIHOSU fit (CAN 108609-96-7) used as a precursor was compounded by US4885401.

[0068]

[Formula 18]



[0069]

the bottom of churning of HOSUFITTO(CAN 108609-96-7) 25.69g (34.5 millimol) and triethylamine 8.1g -- toluene 100ml -- it dissolved in inside. this solution -- gradually -- 40 degrees C -- toluene 100ml -- it dropped in the inner clo ROHOSU fit (CAN 72310-28-2) 8.0g (35.6 millimol)

solution. After addition was completed, the temperature up was carried out to the room temperature, and, subsequently this mixture was heated at 60 degrees C for 3 hours. After cooling to a room temperature, the solid-state to produce was carried out the ** exception, and was discarded. The solvent was removed under the vacuum and the residue was stirred with pentane 200ml. The solid-state produced in that case was isolated, and it washed by the acetonitrile, and was made to dry under a vacuum. Yield of 20.2g (63%).

[0070]

^1H NMR(C7D8) δ =7.2-6.2 (14H, Ar-H), 3.5-3.0 (12H, OMe), 1.4-0.9 (36H, tBu)
 δ = 134.108 ppm (C7D8) of $^{31}\text{P}\{^1\text{H}\}$ NMR.

[0071]

Example 2

Composition of Ligand Ia

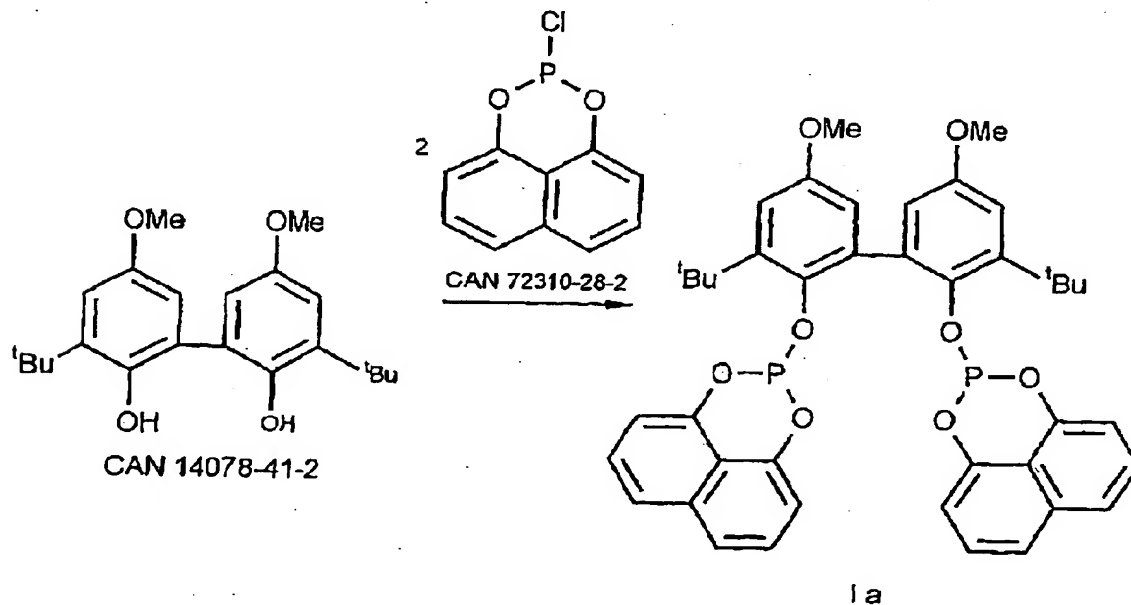
3 and 3'-G t-butyl -2, 2'-dihydroxy -5, and 5'-dimethoxy biphenyl 9.50g (26.5 millimol) -- triethylamine 12.50g -- toluene 110ml -- it dissolved in inside. this solution -- less than 1 hour -- 11.96g (CAN 72310-28-2) (53.3 millimol) of clo ROHOSU fit components -- toluene 100ml -- it dissolved and added to inside. This solution was stirred after termination of addition for further 3 hours, and the triethyl ammonium chloride which carries out deposit precipitation was carried out the ** exception, and concentration hardening by drying of the solution was carried out. The BISUHOSU fit Ia (49% of yield) was obtained from the acetonitrile after recrystallization.

[0072]

^1H NMR(C7D8) δ =7.2-6.4 (16H, Ar-H) and 3.9- 3.7 (6H, OMe) and 1.15 (18H, tBu)
 δ = 105.9 ppm (C7D8) of ^{31}P NMR(s).

[0073]

[Formula 19]



[0074]

Example 3

The hydroformylation of 1-octene

It carried out in the 300ml autoclave (Berghof) for laboratories equipped with the capillary tube for taking out a sample for a trial during an internal thermometer and a reaction. Some of olefins and solvents were inserted in in the autoclave, the catalyst which consists of a Rh-precursor and ligand was dissolved in the remainder of a solvent, and it added from the pressure buret (Druckbuerette) for initiation of a reaction. In all autoclave tests, the nonoic acid rhodium was used as a Rh-precursor.

[0075]

1-octene 60g in toluene 100g was hydroformylated in this type of autoclave. The result is summarized in the following tables.

[0076]

[Table 1]

例番号	B3-1	B3-2	B3-3	B3-4
リガンド番号	3.a	3.a	3.a	3.a
温度 [°C]	100	100	100	100
L/Rh [モル/モル]	5	4	5	8
合成ガス圧[バール]	20	20	50	20
Rh濃度 [ppm]	41	41	43	44
オレフィン反応率	91.5	92.3	94.7	93.2
アルデヒド分析				
ノナナール	81.9	85.1	81.5	84.4
2-メチルオクタナール	15.8	13.5	17.2	13.8
3-エチルヘプタナール	2.0	1.3	1.3	1.5
4-プロピルヘキサナール	0.3	0.1	0.0	0.3

[0077]

Example 4

The hydroformylation of the mixture of octene

60g (1-octene 3.1%, 2-octene 49.0%, 3-octene 33.0%, 4-octene 14.9%) of mixture which consists of octene dissolved into toluene 100g in the autoclave indicated by Example 3 was hydroformylated. A reaction is pursued by sampling and the result 8 hours after reaction time is summarized in the next table.

[0078]

[Table 2]

例番号	B4-1	B4-2
リガンド番号	3.a	3.a
温度 [°C]	130	130
L/Rh [モル/モル]	5	5
合成ガス圧[バール]	20	50
Rh濃度 [ppm]	100	100
オレフィン反応率	97.1%	98.0
アルデヒド分析		
ノナナール	57.6	36.8

[0079]

[Table 3]

例番号	B4-1	B4-2
2-メチルオクタナール	27.3	36.2
3-エチルヘプタナール	8.0	13.6
4-プロピルヘキサナール	7.1	13.4

[0080]

Example 5

The hydroformylation of a propene

Propene 30g dissolved into toluene 150g in the autoclave given in Example 3 was hydroformylated. A reaction is pursued by sampling and the result 5 hours after reaction time is summarized in the next table.

[0081]

[Table 4]

例番号	B5-1
リガンド番号	3.a
温度 [°C]	80
L/Rh [モル/モル]	2.5
合成ガス圧[バール]	20
Rh 濃度 [ppm]	41
オレフィン反応率	98%
アルデヒド分析	
ブタナール	70.5
2-メチルプロパナール	29.5

[0082]

Example 6

The hydroformylation of a butene

In the autoclave given in Example 3, butene 10g dissolved into toluene 100g was hydroformylated. A reaction is pursued by sampling and the result 5 hours after reaction time is summarized in the next table.

[0083]

[Table 5]

例番号	B6-1	B6-2	B6-3
リガンド番号	3.a	3.a	3.b
オレフィン	1-ブテン	t2-ブテン	c2-ブテン
温度 [°C]	80	80	80
L/Rh [モル/モル]	2.5	2.5	2.5
合成ガス圧 [バール]	20	20	20
Rh 濃度 [ppm]	60	60	60
オレフィン反応率	95.3%	44.4%	68.0%
アルデヒド分析			
ペンタナール	83.8	24.6	25.8
2-メチルブタナール	16.2	75.4	74.2

[Translation done.]

CLAIMS DETAILED DESCRIPTION

[Translation done.]